

**CLAIMS**

We claim:

1. A method of modifying a zeolite catalyst to increase selectivity of the catalyst for para-isomers in aromatic alkylation reactions, the method comprising dissolving alumina in a phosphorus-containing acid solution, and treating the zeolite with the dissolved alumina solution.
2. The method of claim 1, wherein:  
  
the acid includes inorganic acids containing phosphorus.
3. The method of claim 1, wherein:  
  
the acid includes at least one of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and phosphorus acid ( $\text{H}_3\text{PO}_3$ ) at a concentration of at least 50 by wt% of aqueous solution.
4. The method of claim 1, wherein:  
  
dissolving the alumina includes dissolving the alumina in an excess of the acid.
5. The method of claim 1, wherein:  
  
the alumina is incorporated into the zeolite in an amount of greater than 0.01 gram of alumina per gram of zeolite.
6. The method of claim 1, wherein:  
  
the phosphorus-containing acid solution is used in an amount of at least 0.1 g of phosphorus-containing acid solution per gram of zeolite.

7. The method of claim 1, wherein:

the zeolite catalyst is a ZSM-5-type zeolite catalyst with a silica to alumina ratio of from 25 to 1000.

8. The method of claim 1, wherein:

the treated ZSM-5 zeolite has total pore volume ranging from 0.10 ml/g to 0.20 ml/g.

9. The method of claim 1, wherein:

the modified catalyst has acid sites showing an ammonia desorption ( $\text{NH}_3$ -TPD) peak at 250-350 °C.

10. A method of preparing an alkyl aromatic product comprising:

dissolving alumina in an inorganic phosphorus-containing acid;

treating a zeolite catalyst with the alumina-containing acid solution; and

contacting the treated zeolite catalyst with an aromatic hydrocarbon and an alkylating agent under reaction conditions suitable for aromatic alkylation.

11. The method of claim 10, wherein:

the aromatic hydrocarbon is toluene.

12. The method of claim 11, wherein:

the alkylating agent is methanol.

13. The method of claim 10, wherein:

the zeolite catalyst is a ZSM-5-type zeolite catalyst.

14. The method of claim 10, wherein:

the alumina is incorporated into the zeolite in an amount at least 0.01 gram alumina per gram of zeolite.

15. The method of claim 10, wherein:

the modified catalyst has from about 0.03 to about 0.08 gram of phosphorus per gram of zeolite.

16. A method of preparing a xylene product comprising:

dissolving alumina in a phosphoric acid solution;

treating a ZSM-5-type zeolite catalyst with the alumina-containing phosphoric acid solution; and

contacting the treated zeolite catalyst with an aromatic feed of toluene under reaction conditions suitable for at least one of toluene methylation and transalkylation.

17. The method of claim 16, wherein:

the phosphoric acid solution used in an amount of from about 0.2g to 0.3 g per gram of zeolite.

18. The method of claim 16, wherein:

the alumina is incorporated into the zeolite in an amount of from about 0.01 g/g zeolite to about 0.02 g/g zeolite.

19. The method of claim 16, wherein:

dissolving the alumina includes dissolving the alumina in an excess of phosphoric acid.

20. The method of claim 16, wherein:

the catalyst exhibits greater than 85% para-xylene selectivity of mixed xylenes when used in toluene methylation.

21. The method of claim 16, wherein:

the catalyst exhibits a toluene conversion over a period greater than 500 hours with a loss of conversion of less than 0.5% per day at a substantially constant catalyst bed temperature.

22. The method of claim 16, wherein:

the toluene methylation feed contains water in an amount of at least 0.1 moles per mole of toluene/methanol.

23. The method of claim 16, wherein:

the toluene methylation feed contains hydrogen in an amount of at least 1.0 mole per mole of toluene/methanol.

24. The method of claim 16, wherein:

the reaction conditions include a reactor pressure of at least 10 psig.